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STUDY OF THE HYDROGEN PEROXIDE BASED WHITENING GEL ON THE CORROSION OF DENTAL METALLIC ALLOYS

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ABSTRACT. The corrosion effect of the bleaching gel based on hydrogen peroxide on two types of dental metallic alloys, frequently used as restorative, prosthetic and implants materials was investigated by electrochemical impedance spectroscopy. The anti-corrosive behavior of Co-Cr and Cr-Ni alloys was found very different for the same experimental conditions. The best results were obtained with Co-Cr alloy, recommending the use of this material in dental treatments.

Keywords: *dental alloys, hydrogen peroxide, electrochemical impedance spectroscopy*

INTRODUCTION

Nowadays, the pharmaceutical industry must answer to an increased demand of products that must guarantee the obtaining of the "perfect brilliant white smile", which is not only a social-media and advertising expectation, but also a shifting of the paradigm of practicing dentistry. Consequently, dental bleaching and fluoride treatment agents become popular for esthetic or cosmetic whitening of stained or discolored teeth, but also for prevention of plaque and caries formation [1].

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Thousands of years ago, tooth cleaning and polishing formulations were based on sea-shells, egg shells and bones ground, as active cleaning components. The first esthetic treatment using bleaching agents was reported at the end of 19th century [2, 3]. In our time, whitening process consists in discoloring dentition by exposing it to various oxidizing materials, such as: hydrogen peroxide (H_2O_2) [4-9] or H_2O_2 releasing agents (*i.e.*, carbamide peroxide (CP) [2, 9-12], and sodium perborate) over a period of time, in order to obtain a lighter color of teeth. CP is a very unstable compound and in contact with tissues and saliva will immediately degrade into about one-third H_2O_2 and two-thirds urea, being in fact a source of H_2O_2 [6, 13]. It is well-known that H_2O_2 acts as a strong oxidizing agent leading to the formation of free radicals, reactive oxygen molecules, and anions [5, 13].

The whitening procedure could be applied *in-office* (using power bleaching formula containing high concentration of H_2O_2, about 25% - 35%, for professional use by dentists), [3, 7, 13, 14], *at-home* (using materials furnished by dentists and used by patients at home for bleaching during night) [3, 13], *over-the-counter* (OTC) bleaching (using products available directly to consumers from drugstores for home use, constituting a low cost alternative to traditional bleaching agents, with little clinical evidence on the safety and effectiveness of the whitening results) [3, 13, 14]. Taking into account the advantages and disadvantages of different commercial products, the main challenge for dentists is not only to determine the effectiveness of various tooth-whitening products, but also to keeping patients' safety [14].

In practical life, bleaching agents may come into contact with restorative materials, particularly when using mouth guard bleaching or home kits [4] causing undesirable changes, such as softening and degradation by wear and corrosion of the teeth and/or restorative materials [10, 13] prosthetic and implant systems [15]. In this context, extensively research were performed in order to evaluate the surface properties and/or surface alterations of different esthetic restorative materials by different methods, such as: surface roughness measurements [2, 4, 11]; surface topography evaluation by scanning electron microscopy (SEM) [2, 8, 11] or by atomic force microscopy (AFM) [7]; profilometric analysis [12]; determination of the alterations in atomic weight by energy dispersive X-ray spectroscopy (EDS) [2, 10] or by X-ray photoelectron spectroscopy (XPS) [9]; metal ions release from dental alloys by inductively coupled plasma-mass spectrometry (ICP-MS) [4]; crystallinity index analysis by Raman spectroscopy [5, 7]; color measurements by spectrophotometry [5, 7]. The corrosion parameters obtained by using electrochemical techniques of investigation of dental metallic alloys in contact with whitening agents are related to the biocompatibility and long-life of different restorative, prosthetic and/or implant systems [4].

Hydroxyapatite is a main inorganic component of bones and teeths, with very excellent biocompatibility. The presence in the studied matrix is due to its properties as promoter of the osteosynthesis in case of small damages of the enamel of tooth [12b].

Until now, for the best of our knowledge, the corrosive effect of these agents (containing H_2O_2) on dental metallic materials has not been well documented. The aim of this work was to present the preliminary data obtained by investigating the corrosive effect of a H_2O_2 based whitening gel product on two types of metallic alloys extensively employed in dentistry (*i.e.*, Co-Cr and Co-Ni), by using electrochemical impedance spectroscopy.

RESULTS AND DISCUSSION

In Figure 1 is presented the electrode surface before and after deposition of the whitening gel used in bleaching treatment of teeth obtained with an optical microscope. The exposure of the metallic interface with whitening gel containing aggressive H_2O_2 lead to affect the integrity of the thin protective oxide passive layer formed at the metallic surface in contact with the air.

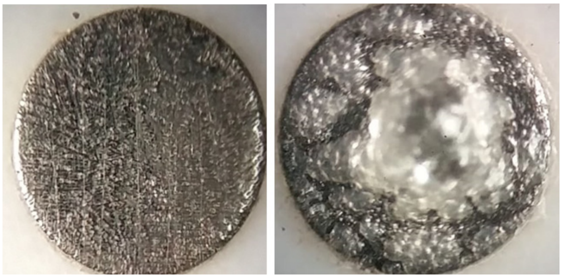

Figure 1. Magnified images (x 400) of Co-Cr and Co-Cr/Gel-Nafion surfaces.

In order to obtain information of the corrosion resistance of the dental alloys (i.e., Cr-Ni, Co-Cr) electrochemical impedance spectroscopy (EIS) measurements were performed on different type of artificial saliva - electrode interfaces after the stabilization of OCP during 1 hour. EIS data were plotted as Nyquist diagrams. The experimental data were modeled using two standard equivalent circuit model (*i.e.*, $R_s(QR_{ct})$ and $R_s(QR_{ct})(Q_1R_1)$).

The correspondence of the elements of the electric circuit is the following: R_s stands for uncompensated solution resistance, Q called constant phase element stands for the double electrical layer capacity and R_{ct} stands for charge transfer resistance, Q_1 and R_1 correspond to constant phase element and resistance of a passive compounds formed at the metallic interface.

The Q value is calculated using the formula $Q = (C_{dl} R_{ct})^{1/n}/R_{ct}$, where: C_{dl} is the capacitance of the double layer and *n* a roughness factor (*i.e.*, n = 1 is the case of a perfectly smooth surface of an ideal capacitor and n = 0 is the case of an ideal resistance) [16].

The value of R_{ct} could be considered as a quantitative parameter, which provides information about the degree of corrosion of the surface or in other words, about the degree of protection of the passive thin oxide film formed on the alloy-electrolyte interface.

The Nyquist diagrams presented in Figure 2 show a semicircle which can be explained by the presence of a surface passive layer, and quantified by a corrosion resistance of this layer. Thus, the R_{ct} values decrease in the order: 55.97 kΩ cm^2 (at Cr-Ni) > 17 kΩ cm^2 (at Cr-Ni/Gel) ≈ 7.2 kΩ cm^2 (at Cr-Ni/Gel-Nafion) and 2.93 kΩ cm^2 (at Cr-Ni/HAP/Gel-Nafion). As expected, the presence of the aggressive H_2O_2 compound in the whitening gel lead to the decrease of the R_{ct} values because of the destruction of the passive metallic oxide film. Even in the presence of HAP, which is less conductive and may constitute an electrons transfer barrier, the elimination of the corrosion processes occurring at metallic interface doesn't take place.

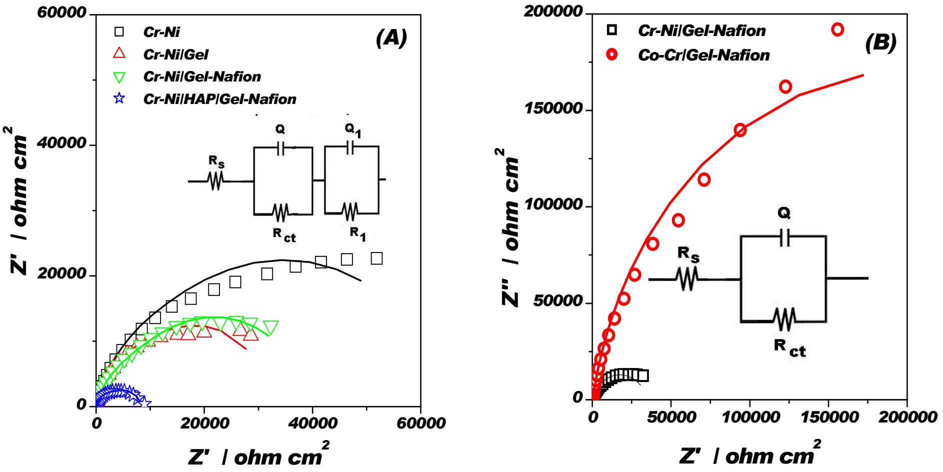

Figure 2. Nyquist diagram of different Cr-Ni modified electrode (see inset) (**A**) and Alloy/Gel-Nafion electrode (**B**) in artificial saliva solution of pH 7 recorded at OCP after 1 h of stabilisation. Experimental conditions: frequencies, 10 kHz - 10 mHz; amplitude, 0.1 V; room temperature. The line corresponds to the fitting curve of the experimental data using the $R_s(QR_{ct})(Q_1R_1)$ (A) and the simplified Randles circuit model $R_s(QR_{ct})$ (B) (see insets).

Comparing the two different metallic specimens (*i.e.*, Cr-Ni and Co-Cr) it can be observed in Figure 3, that the behavior of Co-Cr alloy is quite different than of the Cr-Ni alloy. Using the Randles equivalent circuit, the obtained R_{ct} values are 404.5 kΩ cm^2 in the case of Co-Cr/Gel-Nafion and 35 kΩ cm^2 in the case of Cr-Ni/Gel-Nafion electrode. The difference of magnitude order between time in the two cases could be explained by the well know best anticorrosive behavior of Co-Cr alloy due to a more adherent oxide layer on its surface [17].

Usually the duration of a whitening treatment session is between 30 min to1 hour. For the worst case of electrode's composition (*i.e.* Alloy/ HAP/Gel-Nafion), the influence of time on the R_{ct} value was studied. As seen in Figure 4, for both dental metallic alloy specimens, the increase of contact time with the whitening gel lead to an increase of the R_{ct} values and to the appearance of a slow diffusion process. The parameters resulted by fitting the experimental curve with the $R_s(Q\ R_{ct})$ equivalent circuits are summarized in Table 1.

The analysis of the fitted date gives rise to the observations that in the case of Cr-Ni/HAP/Gel-Nafion electrode an increase of 11 times of the R_{ct} value occurs during 1 hour of contact between whitening gel and Cr-Ni alloy. In the case of Co-Cr/HAP/Gel-Nafion electrode, the same parameter increases only 3 times and remains quasi-constant after few minutes of contact.

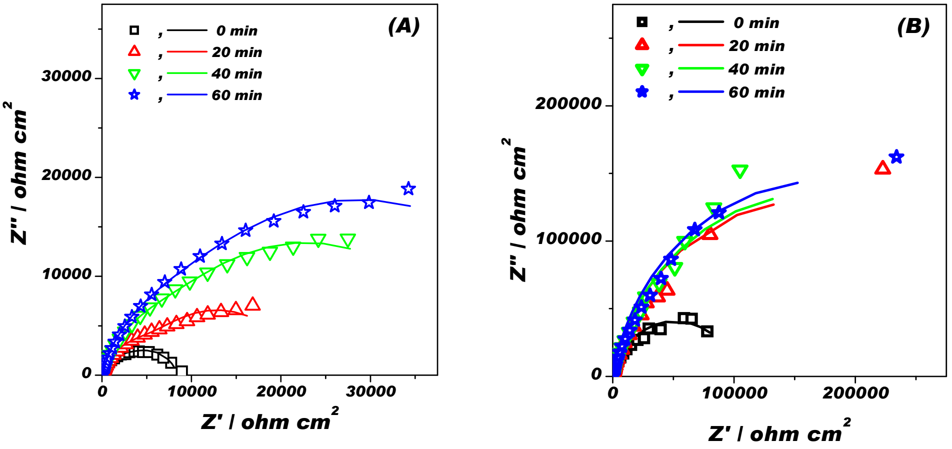

Figure 3. Nyquist diagram of Cr-Ni/HAP/Gel-Nafion (**A**) and Co-Cr/HAP/Gel-Nafion (**B**) electrode at different time (see inset) of exposure to artificial saliva solution of pH 7 recorded at OCP, after 1 h of stabilisation. Experimental conditions: see Fig 2.

Table 1. Fitted EIS parameters of Co-Cr/HAP/Gel-Nafion and Cr-Ni/HAP/Gel-Nafion electrode using $R_s(QR_{ct})$ and $R_s(QR_{ct})(Q_1R_1)$ equivalent circuit models. Experimental conditions: see Fig. 2.

	Co-Cr/HAP/Gel-Nafion				**Cr-Ni/HAP/Gel-Nafion**			
Time/ (min)	0	20	40	60	0	20	40	60
R_s (Ω cm^2)	33.51 ± 2.13	32.87 ± 3.05	34.52 ± 2.11	36.55 ± 3.82	40.32 ± 1.3	39.72 ± 0.8	44.51 ± 0.83	43.99 ± 0.81
Q (S s^n/cm^2)	4.75 10^{-5} ± 1.85	4.28 10^{-5} ± 2.46	4.29 10^{-5} ± 1.59	3.86 10^{-5} ± 2.94	8.19 10^{-5} ± 1.4	38.82 10^{-5} ± 2.9	18.86 10^{-5} ± 4.9	22.9 10^{-5} ± 3.76
n	0.855	0.877	0.869	0.886	0.870	0.819	0.839	0.829
R_{ct} (kΩ cm^2)	102.8 ± 4.33	325.8 ± 12.29	331.2 ± 7.53	345.6 ± 12.78	2.93 ± 4.42	16.29 ± 1.5	42.59 ± 2.22	32.68 ± 1.7
Q_1 (S s^n/cm^2)	-	-	-	-	26.9 10^{-5} ± 4.4	10.61 10^{-5} ± 9.08	12.59 10^{-5} ± 3.6	12.08 10^{-5} ± 2.17
n	-	-	-	-	0.814	0.837	0.843	0.843
R_1 (kΩ cm^2)	-	-	-	-	5.46 ± 2.6	5.53 ± 2.3	9.49 ±6.7	8.06 ± 4.4
chi^2	4.96 10^{-3}	1.71 10^{-3}	5.06 10^{-3}	1.73 10^{-3}	1.45 10^{-3}	0.74 10^{-3}	0.79 10^{-3}	0.71 10^{-3}

± relative standard error (RSD), expressed in percent (%).

However, the highest values of R_{ct} in the case of Co-Cr/HAP/Gel-Nafion electrode indicate good anti-corrosive behavior and an important surface topography alteration [11] in the case of Cr-Ni/HAP/Gel-Nafion electrode. The instability of the gel film on the surface of Cr-Ni/HAP/Gel-Nafion electrode may be also a reason of this behavior, the initiating of a slow diffusion process being more visible than in the case of Co-Cr/HAP/Gel-Nafion electrode(see Fig 4A-B), in the studied range of frequencies. The Chi-square distribution test (χ^2) having value between 10^{-2} - 10^{-3} indicates good agreement between the experimental data and the used equivalent circuit [18, 19].

CONCLUSIONS

Knowing that the bleaching agents may cause structural changes on restorative, prosthetic and implant metallic materials leading to compromise their physical properties and to a premature failure of the treatment, a study of corrosion process of two dental metallic alloys (Cr-Ni and Co-Cr) when in contact with a H_2O_2 based whitening gel were realised.

The electrochemical impedance spectroscopy data reveal that the presence of Gel and even of HAP on the metallic surface lead to a decrease of the corrosion resistance probably due to the destruction of the protective passive metallic oxide film by the aggressive oxidant agent.

In the case of Alloy/Gel-Nafion and Alloy/HAP/Gel-Nafion electrode, the Co-Cr alloy show a better anticorrosive resistance comparing with the Cr-Ni alloy, recommending the first material for its use in restorative, prosthetic and implant treatments.

EXPERIMENTAL SECTION

Reagents

Two specimens of dental metallic alloys were purchased by MESA di Sala Giacomo & C S.n.c. Their content was for Ni-Cr: Ni 63%, Cr 25%, Mo 10%, Si 1.5%, others Mn, Al, Zr, Ce, La, and for Co-Cr: Co 65%, Cr 29%, Mo 5%, C 0.4%, Si 0.35%, Mn 0.25%.

Because it is quite impossible to obtain an artificial saliva solution which replicates the really complex matrix of natural saliva, a receipt proposed by Mondelli [20] was prepared by using appropriate quantities of the following salts: NaCl (0.5 g/L), KCl (0.5 g/L), $CaCl_2*2H_2O$ (0.795 g/L), $NaH_2PO_4*H_2O$ (0.78 g/L), urea (1 g/L), $(NH_4)_2SO_4$ (0.3 g/L), $NaHCO_3$ (0.1 g/L) supplied from Sigma Aldrich and “Reactivul” Bucuresti.

White dental Beauty NOVON® enhanced formula gel for professional use (Gel), containing 6% was obtained from Optident Ltd.

Nafion® perfluorinated resin solution (5 wt. % in lower aliphatic alcohols and water) from Sigma Aldrich was diluted to a concentration of 3 % in ethanol.

All solutions were prepared in distilled water. The chemicals of analytical purity were used as received without any purification.

Electrochemical Methods

Electrochemical impedance spectroscopy measurements were performed using an AutoLab potentiostat (PGSTAT302N EcoChemie, Utrecht, Netherlands) controlled by FRA 2.1 software. The conventional electrochemical cell contains a working electrode of modified dental metallic Ni-Cr and Co-Cr alloys, an Ag/AgCl, KCl_{sat} reference electrode and a platinum wire auxiliary electrode.

For corrosion tests, prior to measurements, the electrodes were stabilized 1 hour under open circuit conditions for recording the open circuit potential (OCP). Impedance spectra on the modified dental Ni-Cr and Co-Cr alloys electrodes were recorded at the OCP value, by using an AC signal with amplitude of ±10 mV and a frequency interval from 10 kHz to 0.01 Hz. Using an equivalent electric circuit, the experimental impedance data were fitted using ZSimpWin 3.21 software. The values of circuit components were subsequently correlated with the processes occurring in the electrochemical cell.

The pH of the electrolyte solutions was adjusted using a glass combined electrode (HI 11310) connected to a pH-meter (type MV 870, Pracitronic, Germany).

Preparation of alloys modified electrodes

The dental Ni-Cr and Co-Cr metallic alloys as cylinders samples, were cut into small pieces to a reduced size of 3 mm diameter and introduced into a Teflon tube, allowing just a controlled surface of 0.0765 cm^2 to be exposed to the artificial saliva solution. Before modification or testing, the metallic alloys electrodes were mechanically cleaned with silicon carbide papers of 500, 800, 1000 grids and then well-rinsed with distilled water and dried. A quantity of whitening gel was drop on the clean electrode surface and dried in air for obtaining the Alloy/Gel interface. For immobilizing the gel on the metallic electrode interface, 3 μL of Nafion 3% was deposited on Alloy/Gel interface and evaporating the solvent by drying in air, obtaining the Alloy/Gel-Nafion electrode. The metallic surface was covered by dropping 5 μL suspension of hydroxyapatite (3 mg HAP in 1 ml distillated water) and then dropping the same volumes of Gel and Nafion, in order to obtain the Alloy/HAP/Gel-Nafion modified electrode. Between each step of covering the evaporation of solvent was expected.

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